MISSOURI DEPARTMENT OF NATURAL RESOURCES
AIR AND LAND PROTECTION DIVISION
ENVIRONMENTAL SERVICES PROGRAM
Standard Operating Procedures

SOP #: MDNR-WQMS-016 EFFECTIVE DATE: May 27, 2005

SOP TITLE: Field Analysis for Total Residual Chlorine

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SUMMARY OF REVISIONS: Not applicable. This is a new SOP.

APPLICABILITY: The procedures described in this SOP are applicable to all ESP and regional office personnel who conduct field analysis of Total Residual Chlorine.

DISTRIBUTION: MoDNR Intranet
ESP SOP Coordinator

RECERTIFICATION RECORD:

Date Reviewed				
Initials				

1.0 SCOPE AND APPLICABILITY

This SOP describes the procedures to be followed by Environmental Services Program (ESP) personnel and regional office field staff, when conducting field analysis of Total Residual Chlorine (TRC). Although Standard Methods, 20th Edition, outlines several different methods to analyze residual chlorine, only an equivalent of the DPD (N,N-diethyl-*p*-phenylenediamine) Method (4500-Cl G) will be discussed here. This method uses the Hach Pocket Colorimeter II Chlorine test kit (Appendix A).

2.0 BACKGROUND

2.1 Virtually all wastewater carries pathogenic microorganisms. Destruction and removal of these organisms occurs throughout the various treatment processes such as sedimentation and filtration, natural die-off, and introduction of chemicals. Chlorinating wastewater, the most common disinfecting process, serves to disinfect and remove remaining pathogenic microorganisms from the effluent before discharge into the receiving stream.

2.2 Total Residual Chlorine can cause adverse effects on fish and other aquatic organisms of the receiving stream. Some aquatic life, such as salmon, trout and other similar fish, can be affected by TRC at levels as low as 0.01 mg/L. This prompted regulating agencies to require the removal of residual chlorine prior to discharge from the treatment facility.

2.3 Facilities disinfecting with chlorine are required, as part of NPDES requirements, to monitor TRC levels in effluent. Improvements in field monitoring equipment, has allowed for accurate field measurements of TRC at lower detection limits.

2.4 Chlorine can be present in water as free chlorine and combined chlorine. Both forms may be present in the same solution and together equal Total Residual Chlorine. Free chlorine is present as hypochlorous acid or hypochlorite ion. Combined chlorine is a combination of chlorine containing compounds including monochloramine, dichloramine, nitrogen trichloride, and other chloro derivatives. The combined chlorine oxidizes triiodide ion to iodine. The iodine and free chlorine react with DPD to form a red solution. The color intensity is proportionate to the total chlorine concentration.

3.0 HEALTH AND SAFETY REQUIREMENTS

3.1 The sample collector shall use an appropriate level of personal protection based on the specific work being done. The minimum level of personal protection is protective gloves and safety glasses. A more stringent level of protection may be required, such as those outlined in a site specific Health and Safety Plan, etc.

3.2 Field personnel shall participate in the medical monitoring program in accordance with MDNR's medical monitoring policy. Those personnel routinely exposed to wastewater of domestic origin should be vaccinated for Hepatitis A as described in MDNR's Hepatitis A Prevention vaccine policy. This policy can be viewed on MDNR's intranet Health and Safety information page.

4.0 PERSONNEL QUALIFICATIONS

Field personnel shall have a working knowledge of the field sample collection procedures and will have at a minimum either attended the department-sponsored inspection and enforcement training or received training from an MDNR employee knowledgeable of the proper sample collection procedures.

5.0 SAMPLING CONSIDERATIONS

Low levels of chlorine quickly dissipate from water due to agitation, exposure to light, and increased temperature. For this reason laboratory analysis is not recommended and all analyses shall be performed on site, immediately following collection.

6.0 SUPPLIES AND EQUIPMENT

The following supplies and equipment are needed for determination of Total Residual Chlorine.

- Sample collection container
- Kimwipes
- Nitrile gloves
- Hach Pocket Colorimeter II for chlorine analysis (see Appendix A)
- Sample cells (see Appendix A)
- DPD Total Chlorine Powder Pillows (see Appendix A)

7.0 PROCEDURE

7.1 Calibration

The instrument is factory calibrated and ready for use without user calibration. A precision check procedure (described in 7.2) should be conducted each day that analysis is to be performed. See 7.2.7 if precision check fails.

7.2 Precision check using Spec√ Secondary Standards

7.2.1 Wipe colorless Spec√ blank cell with a Kimwipe to remove any fingerprints or dust. Place the colorless Spec√ blank into the cell holder with the diamond facing the keypad. Tightly cover the cell with the instrument cap.

7.2.2 Press ZERO/SCROLL. The display will show "0.00".

7.2.3 Wipe colorless Spec√ STD1 cell with a Kimwipe to remove any fingerprints or dust. Place the STD1 cell into the cell holder. Tightly cover with the instrument cap.

7.2.4 Press READ/ENTER. Record the concentration measurement.

7.2.5 Repeat steps 7.2.3 – 7.2.4 with cells labeled STD2 and STD3.

7.2.6 Compare these measurements with control values (recorded on sticker inside the lid of the secondary standard container) to verify the instrument is performing consistently. The acceptable tolerance range for each standard is listed on the sticker and certificate of analysis included with the standards.

7.2.7 If precision check shows inconsistent readings, repeat check following steps 7.2.1-7.2.5. If readings still vary, reference the user instruction manual for further information.

7.3 Collect sample in sample collection container.

7.4 Fill a 10-mL cell (Appendix A) with sample to the 10-mL line and cap. DO NOT ADD REAGENT! This sample will serve as the blank. Carefully, using Kimwipes, wipe excess liquid and fingerprints from cell.

7.5 Press POWER key to turn meter on. An arrow should indicate the instrument is set to the low range channel (LR). If not, refer to instruction manual for directions on how to change the range.

7.6 Remove the meter cap. Place the cell in the cell holder with the diamond mark facing the keypad. Fit the meter cap over the cell compartment to cover the cell.

7.7 Press ZERO/SCROLL. The display will show "- - - -" then "0.00". Remove the blank from the cell holder.

7.8 Fill a second 10-mL cell to the 10-mL line with sample.

7.9 Add the contents of one DPD Total Chlorine Powder Pillow (Appendix A) to the sample cell.

7.10 Cap and shake gently for 20 seconds. A pink color will develop if chlorine is present.

7.11 For Total Residual Chlorine, place the prepared sample in the cell holder and cover the cell with the instrument cap.

7.12 To ensure complete reaction, wait three to six minutes. Press READ/ENTER. The instrument will show "- - - -" followed by the results in mg/L chlorine. If the result is larger than 2.00 and is flashing, the result is above the low range, see note below.

7.13 Total Residual Chlorine results should be recorded in field book and on the Chain of Custody record in the "Other" box of the field parameter section. The parameter name, value and units shall be recorded on the Chain of Custody.

NOTE: The above procedure is for Low Range TRC analysis. If High Range analysis is needed, refer to the instruction manual for procedure.

8.0 INTERFERENCES

8.1 Highly colored samples and turbidity may give inaccurate readings.

8.2 The following substances may interfere at the indicated levels.

- Acidity: greater than 150 mg/L $CaCO_3$. Full color may not develop or color may fade instantly.
- Alkalinity: greater than 250 mg/L $CaCO_3$. Full color may not develop or color may fade instantly.
- Bromine: all levels.
- Hardness: levels greater than 1000 mg/L $CaCO_3$.
- Iodine: all levels.
- Oxidized Manganese or Oxidized Chromium: all levels.
- Monochloramine: will cause a gradual drift to higher readings.
- Ozone: at all levels.

8.3 If total chlorine residual is in high enough concentration, the DPD can bleach out and no color will develop resulting in a false negative reading (See NOTE under section 7.0). Other false negatives can not be verified in the field and would require further laboratory testing so results should be recorded as is.

8.4 If interference resulting in a false positive is suspected, a chlorine free sample can be created by one of the following methods, and tested to confirm interference. If the reading remains elevated it is likely an interfering substance is present. This should be

noted in the field notes and taken into consideration when reporting results on the Chain of Custody.

8.4.1 Take sample and agitate the water for a few minutes to dissipate the chlorine. Retest the sample.

8.4.2 Add a tablet of Sodium Thiosulfate to the sample. Shake to dissolve the tablet. Retest the sample.

9.0 QUALITY CONTROL

9.1 Field calibration is not required due to factory calibration. A precision check shall be conducted prior to field analysis.

9.2 The ESP meters are subjected to monthly QC checks. Accuracy is checked, by WQMS personnel, using a known certified standard solution.

10.0 REFERENCES

California State University, Sacramento, Department of Civil Engineering, *Operation of Wastewater Treatment Plants, volume 1,* 1998

Hach Company, *Pocket Colorimeter II Analysis System Chlorine (Cl_2) Instruction Manual*, 2003

Standard Methods for the Examination of Water and Wastewater, 1998, 20th edition.

Chlorine Monitoring and Dechlorinating Techniques Handbook,
http://www.gvrd.bc.ca/water/chlorin/hndbkchlormonit.pdf

Appendix A

Pocket Colorimeter II

Sample Cell for colorimeter

DPD Total Chlorine Powder Pillows